



### What are SiAlON Ceramics?

**SiAlONs are ceramic alloys** based on the elements **silicon** (Si), **aluminium** (Al), **oxygen** (O) and **nitrogen** (N) and were developed in the 1970s to solve the problem of silicon nitride ( $\text{Si}_3\text{N}_4$ ) being difficult to fabricate.

As alloys of  $\text{Si}_3\text{N}_4$ , **SiAlONs** exist in three basic forms. Each form is iso-structural with one of the two common forms of  $\text{Si}_3\text{N}_4$ , beta ( $\beta$ ) and alpha ( $\alpha$ ) and with silicon oxynitride. The relationship between that of SiAlON and  $\text{Si}_3\text{N}_4$  is similar to that between brass and pure copper. In the later case, copper atoms are replaced by zinc to give a better and stronger alloy than the mother metal. In the case of

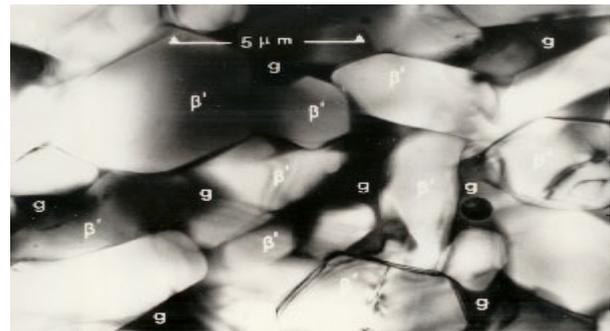
SiAlON, there is substitution of Si by Al with corresponding atomic replacement of N by O, to satisfy valency requirements. The resulting 'solution' (SiAlON) has superior properties to the original pure solvent (silicon nitride).

The fundamental structural unit of  $\text{Si}_3\text{N}_4$  is the  $\text{SiN}_4$  tetrahedron, which is analogous to the  $\text{SiO}_4$  structural units in silicates. The tetrahedra are linked together into a rigid three dimensional framework by sharing corners. The Si-N bonds are short and they are very strong. This strong, rigid, compact structure is responsible for many of the important properties of  $\text{Si}_3\text{N}_4$ .

### $\beta$ -SiAlON Ceramics

$\beta$ -SiAlON is based upon the atomic arrangement existing in  $\beta$ - $\text{Si}_3\text{N}_4$ . In this material, Si is substituted by Al with corresponding replacement of N by O. In this way up to two-thirds of the silicon in  $\beta$ - $\text{Si}_3\text{N}_4$  can be replaced by Al without causing a change in structure. The chemical replacement is one of changing Si-N bonds for Al-O bonds. The bond lengths are about the same for the two cases but the Al-O bond strength is significantly higher than that of Si-N. In SiAlON the Al is co-ordinated as  $\text{AlO}_4$  and not as  $\text{AlO}_6$  as in alumina ( $\text{Al}_2\text{O}_3$ ). Therefore, in  $\beta$ -SiAlON the bond strength is 50% stronger than in  $\text{Al}_2\text{O}_3$ . Thus SiAlONs intrinsically have better properties than both  $\text{Si}_3\text{N}_4$  and  $\text{Al}_2\text{O}_3$ .

$\beta$ -SiAlON has the general formula  $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$  where z varies between 0-4.2 and requires a sintering additive such as yttria ( $\text{Y}_2\text{O}_3$ ), magnesia ( $\text{MgO}$ ) or a rare earth oxide in order to densify. As a solid solution, the vapour pressure of  $\beta$ -SiAlON is lower than that of  $\text{Si}_3\text{N}_4$  and as a result the SiAlON will form more liquid at a lower temperature.  $\beta$ -SiAlON is thus more easily densified than  $\text{Si}_3\text{N}_4$  using normal sintering techniques. Furthermore, it should be noted that the lower vapour pressure of SiAlON reduces decomposition at high temperatures so that the SiAlON is thermodynamically more stable than  $\text{Si}_3\text{N}_4$ .



The  $\beta$ -SiAlONs produced by **International Syalons** use yttria as a sintering aid. When sintered above  $1700^\circ\text{C}$  elongated hexagonal shaped  $\beta$ -SiAlON grains (see the image above) are precipitated and grow in the oxynitride liquid phase formed from the sintering additives such as yttria, alumina, silica and aluminium nitride. Subsequently, on cooling the liquid phase forms a refractory intergranular glass. This produces the material **Syalon 101**. This material, with its elongated  $\beta$  grains, is characterised by high strength and toughness.

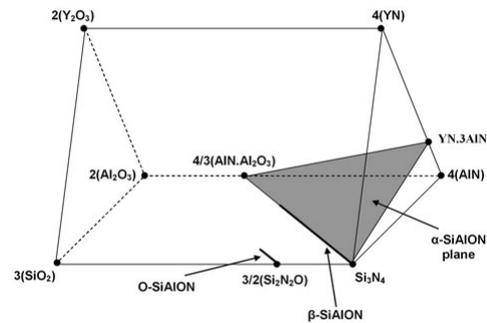
It is possible through controlled processing to convert the intergranular glass to yttrium aluminium garnet (YAG) which is a refractory crystalline phase. This gives the material better high temperature properties and the material can retain its strength at temperatures up to  $1350^\circ\text{C}$ . This material is available as **Syalon 201**.



## $\alpha$ -SiAlON Ceramics

The second form of  $\text{Si}_3\text{N}_4$  with which SiAlON is iso-structural is  $\alpha\text{-Si}_3\text{N}_4$ . The stacking structure in  $\alpha\text{-Si}_3\text{N}_4$  is different from  $\beta\text{-Si}_3\text{N}_4$  in that the long 'channels' which run through the  $\beta$  structure are blocked at intervals. This gives rise to a series of interstitial holes. In each  $\text{Si}_{12}\text{N}_{16}$  unit cell there are two interstitial holes. In  $\alpha\text{-SiAlONs}$ , Si in the tetrahedral structure is replaced by Al with limited substitution of N by O. Valency requirements are satisfied by modifying cations occupying the interstitial holes. In this way cations of yttrium (Y), calcium (Ca), lithium (Li) and neodymium (Nd) for example can be incorporated into the structure. Consequently  $\alpha\text{-SiAlON}$  has the general formula  $\text{Me}_x\text{Si}_{12-(m+n)}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$  where  $x < 2$  and Me is the modifying cation.

The  $\alpha\text{-SiAlON}$  phase region can be illustrated in the following phase diagram, which shows the system based on  $\text{Y}_2\text{O}_3$  additive. This is a Jänecke prism and is the most convenient way to show the five component SiAlON system i.e. Me-Si-Al-O-N. The  $\alpha\text{-SiAlON}$  phase region is the shaded region in the  $\text{Si}_3\text{N}_4\text{-YN}.3\text{AlN-AlN}. \text{Al}_2\text{O}_3$  plane. It can be seen also that the  $\beta\text{-SiAlON}$  solid solution, which extends along the  $\text{Si}_3\text{N}_4\text{-AlN}. \text{Al}_2\text{O}_3$  line, thus forms a border of the  $\alpha\text{-SiAlON}$  plane. This results in the possibility to form mixed  $\alpha:\beta\text{-SiAlONs}$ .



$\alpha\text{-SiAlONs}$  are formed similarly to  $\beta\text{-SiAlONs}$  in that the  $\alpha$  phase is precipitated from an oxynitride liquid phase. During the reaction the amount of liquid is gradually reduced as the modifying cation is incorporated into the  $\alpha\text{-SiAlON}$  structure. Thus, in theory, it is possible to form a single phase  $\alpha\text{-SiAlON}$ . However, in practice some residual intergranular glass will remain after sintering, which as with the  $\beta\text{-SiAlONs}$  can often be converted to refractory crystalline phases. Thus by careful control of the composition and sintering cycle  $\alpha\text{-SiAlON}$  ceramics can be formed with excellent high temperature properties. The  $\alpha\text{-SiAlON}$  grains tend to have a small, equiaxed morphology which results in materials which have a lower strength and toughness than  $\beta\text{-SiAlON}$ . However,  $\alpha\text{-SiAlON}$  has a higher hardness than  $\beta\text{-SiAlON}$ .

## Mixed $\alpha:\beta\text{-SiAlON}$ Ceramics

As described above it is possible to control the starting composition and the processing to develop mixed  $\alpha:\beta\text{-SiAlONs}$ . Thus one can tailor the material to have a combination of the high strength and

toughness of  $\beta\text{-SiAlON}$  and the high hardness and high temperature properties of  $\alpha\text{-SiAlON}$ .

**International Syalons** produce a mixed  $\alpha:\beta\text{-SiAlON}$  which is available as **Syalon 050**.

## O-SiAlON Ceramics

The final form of sialon, O-SiAlON, is iso-structural with silicon oxynitride ( $\text{Si}_2\text{N}_2\text{O}$ ). The structure of  $\text{Si}_2\text{N}_2\text{O}$  consists of layers of  $\text{Si}_3\text{N}_4$  rings joined by Si-O-Si bonds. In O-SiAlON, Al and O replace some Si and N atoms.

International Syalons don't manufacture O-SiAlON ceramics. They are effectively a refractory with no benefits over  $\beta\text{-SiAlON}$  for example, other than cost, although the much superior properties of  $\alpha$ - and  $\beta\text{-SiAlONs}$  provide much greater service life, thus offsetting any supposed cost benefits.

